Netsu Sokutei **20**(1)7-18

論 文

The Equation of Motion and Conservation of Energy in Open Systems

Marek Danielewski

(Received October 6, 1992)

The new possibilities arising from the quantitative description of the dynamics of heat and mass transport are presented. The new postulated form of the momentum flux is applied in a general case of transport in continuum (homogeneous multicomponent system in nonequilibrium). This approach results in:
i) conservation equations in a viscous, compressible media (the equation of motion and the internal energy conservation equation), the simplified formulas for ii) "ideal compressible media (showing negligible both, diffusivity and viscosity) and, the equations of motion for the isothermal transport in iii) multicomponent solids and gases. It is shown that, in the non-viscous compressible medium, the I law can be derived from the postulated formulas. The conservation equations and appropriate expressions defining the fluxes of mass, momentum and heat, allow a quantitative description of a nonreversible process to be obtained.

The presented phenomenology emphasizes i) the limitations of the second Fick's and Fourier's laws and suggests ii) the directions of practical applications of this phenomenology in the development of the new experimental methods.

INTRODUCTION

The more experienced reader may skip the first section. The concepts presented it are recognized by several authors.

For a majority of chemists, the equation of motion sounds almost like a mystery. It is hardly surprising though. The two most successful (mainly in hydrodynamics) forms of the equation of motion (ME, *i.e.* the mathematical formula of momentum conservation in continuum) are almost useless in chemistry. They are not even being mentioned in a majority basic courses of the physical chemistry.

The cause of such a status (of the theory of transport in chemistry) is simple in fact. The mathematical theory of the Navier-Stokes equations (N-S) is not complete[1]. The well-known Euler's equation is inadequate when used in majority of real systems (e.g. in the case of mass transport in solids). Thus it can be formally questioned whether these equations really describe general flows. Finally the missing proof of uniqueness of the N-S equations and mathematical problems in their practical applications, all of them wholly and very effectively discourage chemists in using them. Consequently chemistry does not have any decent formula that would allow to establish a successful link with mathematics (and physics), formula which would allow a more advanced mathematical modelling.

In some very limited situations the Onsager relations have a practical value. However unless the number of unknown coefficients can be reduced, the formalism becomes essentially useless from a practical standpoint. Author disagree with the deep underlying interpretation of the minimum entropy production and thermodynamic coupling. The thermodynamics of open systems has to be better understood before further

---

Department of Chemical Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152, Japan. On leave from School of Mining and Metallurgy, Faculty of Materials Science and Ceramics, Al. Mickiewicza 30, 30-059 Cracow, Poland

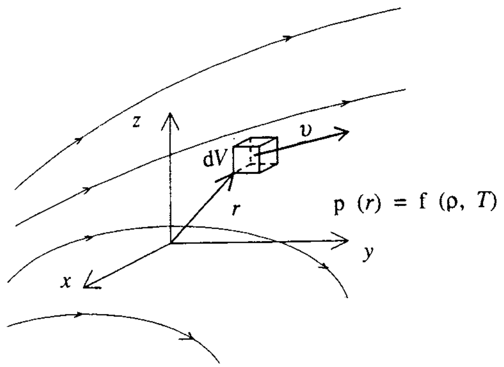
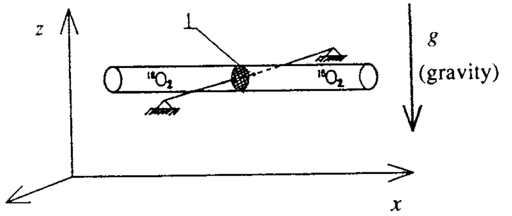
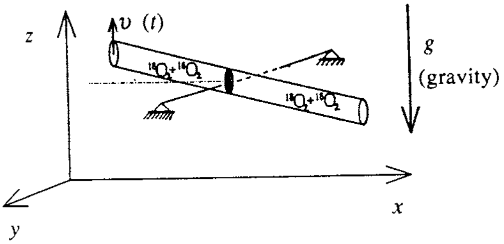


Fig. 1 The imaginary, elementary volume element dV at position r (position defined in a laboratory, *i.e.* external, reference frame, ERF), the medium moves relative to the ERF, ***e.g.*** drifts with local velocity $v(v_x, v_y, v_z)$ (at the same position r).



(a) $t = t\ (O^+),\ v = 0$



(b) $t > 0,\quad v \neq 0$

Fig. 2 The interdiffusion process between O^{16} and O^{18}, the container is divided into two parts by the permeable membrane (1). The container is positioned on the torque suspension which position is determined by its initial, $t(O^+)$, centre of mass (a). The interdiffusion process in progress, $t>0$, as the container mass centre position is a function of time, the time dependent distortion from the initial position follows (b).

development of this rule. The basic assumption of rational thermodynamics about existence of entropy in nonequilibrium is not yet clear and, in particular it can not be applied to open (the mass exchanging) systems[2)].

Why the equation of motion is such a necessity? Take any medium (fluid, gas, solid or their mixture), the mixture it is in nonequilibrium and surrounds an observer (or it is fixed, *e.g.* in a chemical reactor). In general in such an open system the number of coupled processes occurs. In order to describe entirely such a system, Fig. 1, we ought to know (to calculate and/or measure) the temperature, density (or any combination of p, ρ and T) and local velocity of the medium, v. The velocity is a vector quantity $[v\ (v_x,\ v_y,\ v_z)]$ thus, we do always have five unknown parameters (two less in unidimensional systems). Formally, unless the number of equations equals the number of unknown parameters, the quantitative calculations are not possible. This basic rule of mathematics invariably holds. However, situation is not hopeless.

The chemical systems must obey the following conservation laws: i) the law of mass conservation (the mathematical formula of this law is called the equation of continuity), ii) the law of energy conservation* and, iii) the law of momentum conservation (*i.e.* the equation of motion, which is a vector equation and, consequently is equivalent of three scalar equations). Thus, if the equations are correct, their number balances the number of the unknown parameters and any problem can be quantitatively solved.

There is another commonly used method. The experiments might be arranged in such a way that the movement (drift) becomes negligible. Is this an effective solution?

The mixing process is one of the simplest chemical reactions studied. Let us take the two oxygen isotopes (O^{18} and O^{16}). They can be fixed into a container in which we have an permeable membrane which avoids mechanical agitating but does not affect inter-diffusion (mixing), Fig. 2(a). The container is then situated, exactly at its centre of mass, on some sensitive torque

---

*In some limited situations the II Fick's and Fourier's laws are sufficient in describing a quasi-stationary processes. These formulas represent the retarded forms of the general conservation equations.

suspension. What can be measured now? All energetic effects are negligible. In the same time it is evident that the container which once was stable [at the very beginning of the reaction, $t = t(O^+)$] will start to fall down to the right side, Fig. 2(b). The diffusion will affect the centre of mass position and unless the effect is compensated by any external forcing (*e.g.* microbalance) the stability will be lost. The movement starts and, *e.g.* we should like to know the container velocity changes as a function of time. It is evident that the same effects occur during nonuniform heating, interdiffusion in solids, reactive diffusion and so on. These effects, instead to be avoided, can be used as a source of the valuable information.

The author's approach has been stimulated by the Darken's concept of drift velocity in solids[3] and by the Holly's model of the free fluid[4]. If the diffusional transport in solids can results in the local production of the drift velocity[3] hence the analogous processes in fluids and gases are obvious. The local accumulation of heat energy in solid (in all media in general) can as well result in solid local expansion (*i.e.* the drift production process). Accordingly any form of transport process within a medium which affects the local properties of matter can result in drift generation.

Some analytical technic (taking advantage of such mechanical movement) have been already developed. The measurements of the propagation rate of the heat waves in solids, *e.g.* utilising two lasers (as a heat source and detector) allows the simultaneous measurements of thermal-conductivity and mechanical properties.

The tremendous progress of the most experimental technic will tell many other practical experimental possibilities. However to do this it is necessary to have a complete set of equations. Otherwise one will always calculate an "effective values" (What frequently means: we do not know exactly what's going on here).

Using the new phenomenological description of the energy and momentum transport in continuum[5], the paper presents an extended analysis of the mathematical formula describing the global energy balance which results from this approach.

The notation used follows actual evolution in applied mathematics (as well as non-reversible thermodynamics) and allows the physical interpretation of all the formulas. Whose not familiar with such a formulas should only remember that the divergence (Div or div) is the difference between amount of any arbitrary quantity going in and out of the elementary volume (it does not depend on the choice of the reference frame, i.e. div (in any external frame of reference, ERF) = div (in IRF). Thus the negative divergence means the balance is positive, i.e. more stay in the volume element than goes out. Than there are gradients (Grad or grad), again they do not depend on our position or movement (on the choice of frame of reference) and describe the distributions of components and velocities, as well as represent an internal forcing. The last two symbols used in the following sections there are two time derivatives: i) the so called Euler's derivative ($\partial/\partial t$, which tells how the arbitrary quantity changes with time in any arbitrary laboratory reference frame, e.g. in the ERF which is shown in Fig. 1) and ii) the substantive derivative (D/Dt, which informs how the same quantity depends on time in the internal reference frame, e.g. when one becomes an internal observer ("an idealistic, utopian, observer" who drifts with the medium and the same time does not "disturb" any of the local processes, neither affects the medium local properties, *e.g.* local density). This last form of the time derivative allows to simplify formulas and, is the key factor in understanding open system (Note, that all processes in the IRF do not depend whatsoever on our choice of external frame of reference, ERF, *i.e.* on laboratory frame of reference).

In most practical applications, the calculations are done using a numerical methods, therefore there's not necessary to know and to discussed them. Again, the key factor in using the precisely defined formulas, is to understand their meaning and formulate the proper initial-boundary value problem. After that the mathematics will do the job.

The essence of presented phenomenology is:
i) the standard definition of the mass flux vector, which is a sum of the diffusional and drift flows (i.e. a first order tensor, where $j_i = q_{m,i}$):

$$\begin{matrix} j_i & = & j_{d,i} & + & \rho_i v \\ \begin{bmatrix}\text{mass flux,}\\ \text{ERF}\end{bmatrix} & = & \begin{bmatrix}\text{diffusional flux,}\\ \text{ERF=IRF}\end{bmatrix} & + & \begin{bmatrix}\text{drift flux,}\\ \text{ERF}\end{bmatrix} \end{matrix} \qquad (1)$$

where υ is a local medium drift velocity and, the ERF and IRF denote the external (*i.e.* laboratory or observer) and internal reference frames, respectively; and

ii) the postulated form of the momentum flux tensor (*i.e.* a second order tensor):

$$\begin{array}{ccccc} \boldsymbol{j}_i & = & \boldsymbol{j}_{\upsilon,i} & + & (\rho_i\,\upsilon_i)\upsilon \\ \left[\begin{array}{c}\text{momentum}\\ \text{flux tensor, ERF}\end{array}\right] & = & \left[\begin{array}{c}\text{momentum flux}\\ \text{due to viscosity,}\\ \text{momentum diffusional}\\ \text{flux tensor, ERF=IRF}\end{array}\right] & + & \left[\begin{array}{c}\text{momentum drift}\\ \text{flux tensor, ERF}\end{array}\right] \end{array} \qquad (2)$$

Upon comparing eqs. (1) and (2), it can be seen that the postulated form of the momentum flux is based on the concept that the flux of this conservative property (momentum) can be treated as the mass flux in continuum. It should be mentioned that the all classical treatments assume that the drift flow of momentum equals $(\rho_i \upsilon_i)\ \boldsymbol{u}$, *i.e.* the momentum is transported by the centre of mass velocity, $\boldsymbol{u}$[6].

The proposed phenomenology relays on a i) unified "*diffusional approach*" to the transport in fluid (in all media in general[7]) and a ii) fundamental uniqueness of the two local average velocities, the medium drift velocity and the diffusional velocity[5].

The work is an attempt to unify the heat and mass transport phenomenology, to narrow the gap between the physico-chemical statements and precise mathematical formulas.

Definitions

Transport is considered in an isotropic continuum in nonequilibrium* (*e.g.* in a fluid, gas or solid). In this system the state variables (local velocities, temperature and concentrations) are assumed to be continuous functions of the space coordinates and of time. It is always understood that the all variables in this nonuniform single-phase system are averaged in the elementary volume at the position $\boldsymbol{r}$ and time t, Fig. 1. The vector $\boldsymbol{r}$ denotes the position of the small element of volume dV. This elementary volume is infinitely small compared to the dimensions of the whole system but large when compared to the mean-free path length of the moving components. Such a medium (*e.g.* fluid) can be called continuous or, thermodynamically, nonuniform single-phase system. The discussed transport phenomena are restricted to systems which are close to equilibrium, *i.e.* it is meant that only the linear derivatives of the variables are important.

The multicomponent system is composed of n chemical species (components) denoted by i, $i = 1, 2, \ldots, n$. The fluxes can be expressed with respect to i) fixed coordinates (in ERF) and ii) with respect to any of the arbitrary velocity (in IRF). The mean velocity of the *ith* component in the elementary volume dV and with respect to an ERF, is given the symbol $\boldsymbol{u}_i$. The average local density (ρ) is a sum of the local partial densities (ρ_i), $\rho = \sum_{i=1}^{n} \rho_i$.

The two mechanisms general to all transport are molecular diffusion and drift transport. Consequently the following characteristic fluxes are defined:

1) The general flux (in ERF) of i that passes through a plane of unit area and normal to the local velocity vector of i (the plane is stationary and has constant dimensions with respect to the ERF):

$$j_i = \rho_i\ \upsilon_i \qquad (3)$$

2) The diffusional flux (which does not depend on the choice of the frame of reference) defines the average local diffusional velocity of component i:

$$j_{d,i} = j_i\,(\text{diff.}) = \rho_i\ \upsilon_{d,i} \qquad (4)$$

3) The drift flux (equivalent to a flow flux in liquids or convection flow in gases) is defined by the average diffusional flux (or diffusional velocity) and by the general flux (the one measured in ERF):

$$j_i\,(\text{drift}) = \rho_i \upsilon = j_i - j_i\,(\text{diff.}) = \rho_i(\upsilon_i - \upsilon_{d,i}) \qquad (1)$$

where $\boldsymbol{u}$ is the local drift velocity of the medium of composition t_i. The drift velocity is common for all the components and consequently from eqs. (1), (3) and (4) it follows that,

$$\upsilon_i = \upsilon_{d,i} + \upsilon \qquad (5)$$

and that the defined fluxes are related to each other

---

*In the case of irreversible phenomena, the system is never uniform throughout. It consist of an infinite number of phases. Thus the continuum in nonequilibrium is defined thermodynamically as nonuniform single-phase system. A discontinuous systems is defined as multiphase or heterogeneous system.

through eq. (1). Thus upon adding all the partial mass fluxes [as defined by the eq. (1)], the total mass flux is given by

$$\boldsymbol{j} = \rho\,\boldsymbol{u} = \sum_{i=1}^{n} \boldsymbol{j}_{d,i} + \rho\ \upsilon = \rho\upsilon_d + \rho\ \upsilon = \boldsymbol{j}_d + \boldsymbol{j}\ \text{(drift)} \qquad (6)$$

where $\boldsymbol{j}_d$ is the average diffusional flux in the elementary volume dV and, $\boldsymbol{u}$ and τ_d denote the centre of mass and the average diffusional velocities, respectively.

Equation (6) defines:

i) the average diffusional velocity

$$\upsilon_d = \frac{1}{\rho}\sum_{i=1}^{n} \boldsymbol{j}_{d,i} \qquad (7)$$

ii) relation between the all defined average velocities

$$\boldsymbol{u} = \upsilon + \upsilon_d \qquad (8)$$

The IRF (*e.g.* the frame of reference which has the velocity equal the local drift velocity of the medium) is associated with the substantive derivative ***D/Dt*** (the Lagrange operator). This is the time derivative of a local quantity taken at the centre of the element d*V* moving with any arbitrary velocity, *e.g.* ***u***. The substantive derivative and partial derivative $\partial/\partial t$ (which is the time derivative taken in the volume d*V* at *r*, *i.e.* with respect to ERF) of a scalar quantity are related by:

$$\left.\frac{\boldsymbol{D}}{\boldsymbol{D}t}\right|_{\upsilon} = \frac{\partial}{\partial t} + \upsilon \bullet grad \qquad (9)$$

We introduce at this point a useful relation (is valid for an arbitrary quantity *a*);

$$\text{div}\ (a\boldsymbol{u}) = a\ \text{div}\boldsymbol{u} + \boldsymbol{u}\cdot\text{grad}a \qquad (10)$$

The above two relations for a vector quantity become

$$\left.\frac{\boldsymbol{D}}{\boldsymbol{D}t}\right|_{\upsilon} = \frac{\partial}{\partial t} + \upsilon \bullet \text{Grad} \qquad (11)$$

$$\text{Div}\ (\boldsymbol{j}\boldsymbol{u}) = \boldsymbol{u}\ \text{div}\boldsymbol{j} + \boldsymbol{j}\cdot\text{Grad}\boldsymbol{u} \qquad (12)$$

where the physical interpretation of all the terms do not differs from the already presented [*e.g.* in the case of a scalar quantities, eq. (9)].

The diffusional fluxes can be expressed by any appropriate formula, *e.g.* by the Fickian formula:

$$\boldsymbol{j}_{d,i} = -\,\boldsymbol{D}_i\ \text{grad}\ \rho_i \qquad (13)$$

where for a non-uniform, non-ideal medium the diffusion coefficient of the *ith* component is its intrinsic diffusion coefficient [in solids[3)]] or in general, the chemical diffusion coefficient of *i*th component.

Conservation of mass

The most general (and not a controversial one) mathematical formula of this law[6)] is called the equation of continuity (CE). It can be derived using the general method (the general means here that equation does not depend on the geometry of elementary volume, which has not to be a simple cubic volume element). Because this general and, well known method, will be used in deriving the other conservation equations, the complete derivation will be shown here. The mass of *ith* component in an arbitrary volume *V* is $\int \rho_i dV$, where the integration is over volume *V*. The rate of mass change in this volume is

$$\frac{d}{dt}\int_V \rho_i dV = \int_V \frac{\partial \rho_i}{\partial t}\, dV \qquad (14)$$

The order of integration and differentiation can be interchanged thus the above identity is always valid. The mass changes in volume *V* as a result of the drift flow, the diffusional flow and as a result of changes in mass due to chemical reactions:

$$\int_V \frac{\partial \rho_i}{\partial t}\, dV = -\int_A \rho_i\, \upsilon \bullet dA - \int_A \rho_i \upsilon_{d,i} \bullet dA + C_i$$

$$\left[\begin{array}{c}\text{mass}\\ \text{change in}\\ \text{the volume}\\ \text{element,}\\ \text{ERF}\end{array}\right] = \left[\begin{array}{c}\text{accumulation}\\ \text{of mass as}\\ \text{a result of}\\ \text{drift flow,}\\ \text{ERF}\end{array}\right] + \left[\begin{array}{c}\text{accumulation}\\ \text{of mass as a}\\ \text{result of dif-}\\ \text{fusional flow,}\\ \text{ERF=IRF}\end{array}\right] + \left[\begin{array}{c}\text{mass change of}\\ \text{the } i\text{th component}\\ \text{as a result of che-}\\ \text{mical reactions,}\\ \text{ERF=IRF}\end{array}\right] \qquad (15)$$

The integral on the right-hand side (r.h.s) of the eq. (15) is performed over the total surface of the volume element, A. The vector normal to the surface d*A* is positive when its direction is oriented outward of the volume element, which results in the minus sign before the integrals on the r.h.s. of eq. (15). The surface integral can be transformed into a volume integral by Green-Gauss'-Ostrogradzki theorem so that eq. (15) becomes

$$\int_V \frac{\partial \rho_i}{\partial t}\, dV = -\int_V \text{div}\,(\rho_i\, \upsilon)\, dV - \int_V \text{div}\,(\rho_i \upsilon_{d,i})\, dV + \int_V C_i{}^{*}\, dV \qquad (16)$$

and can be written in the form

$$\int_V \left[\frac{\partial \rho_i}{\partial t} + \mathrm{div}\,(\rho_i\,\upsilon) + \mathrm{div}\,(\rho_i\,\upsilon_{d,i}) - C_i^* \right] \mathrm{d}V = 0 \qquad (17)$$

Providing the volume is fixed with respect to the ERF, the integrand is zero. Thus the eq. (17) equals zero when

$$\frac{\partial \rho_i}{\partial t} + \mathrm{div}\,(\rho_i\,\upsilon) + \mathrm{div}\,(\rho_i\upsilon_{d,i}) - C_i^* = 0 \qquad (18)$$

Equation (18) is the partial continuity equation in the ERF, where C_i^* is a chemical reaction term (a local sink/source of mass). In the IRF [using relations (9) and (10)], it is:

$$\left.\frac{\mathbf{D}\rho_i}{\mathbf{D}t}\right|_{\upsilon} + \rho_i\,\mathrm{div}\;\upsilon = -\,\mathrm{div}\boldsymbol{j}_{d,i} + C_i^* \qquad (19)$$

After summing all the partial CE, eq. (19), over all i and nothing that mass is conserved in a chemical reaction, the CE for the medium as a whole (in the IRF) results

$$\left.\frac{\mathbf{D}\rho}{\mathbf{D}t}\right|_{\upsilon} + \rho\;\mathrm{div}\;\upsilon = -\sum_{i=1}^{n}\mathrm{div}\,\boldsymbol{j}_{d,i} = -\,\mathrm{div}\sum_{i=1}^{n}\boldsymbol{j}_{d,i} = -\,\mathrm{div}\boldsymbol{j}_{\mathrm{d}} \qquad (20)$$

where the substantive derivative denotes the time dependence of the mass density in the elementary volume moving with a drift velocity υ, *i.e.* in the elementary volume drifting with the medium (in the IRF). Upon combining eqs. (6) and (20), the CE for the medium as a whole takes the well known form

$$\left.\frac{\mathbf{D}\rho}{\mathbf{D}t}\right|_{\mathrm{u}} + \rho\;\mathrm{div}\;\mathrm{u} = 0 \qquad (21)$$

Equations (20) and (21) describe the mass balance in the two different internal frames of reference (are different forms of the local equation of continuity for the medium as a whole). When the drift velocity becomes negligible, eqs. (20) and (21) reduce to so called 2nd Fick's law

$$\frac{\partial \rho}{\partial t} = -\,\mathrm{drv}\boldsymbol{j}_{\mathrm{d}} \qquad (22)$$

Equations (1) and (3)–(21) are well known and commonly accepted mathematical formulas describing the mass transport in all media[6]. In the following sections the new approach to the momentum conservation is presented. The essence of this approach is the postulate that the local flux of momentum is a sum of drift and diffusional fluxes [analogously to the mass flux, eq. (1)]. Except of the momentum conservation, the further analysis will be restricted to the case of a simple, viscous and compressible media.

Conservation of momentum

If $\tau_i\upsilon_i$ is defined as a momentum of the ith component in the volume element, the momentum flux tensor of the ith component ($\boldsymbol{J}_i$) is given by eq. (2)

$$\boldsymbol{J}_i = \boldsymbol{J}_i\ (\mathrm{drift}) + \boldsymbol{J}_i\ (\mathrm{diff.}) = (\rho_i\upsilon_i)\ \upsilon + \boldsymbol{J}_{\mathrm{v},i} \qquad (2)$$

where the first term on the right-hand-side of eq. (2) (r.h.s.) is the drift flow of the momentum in the ERF. The momentum viscous (diffusional) flux (the second term on the r.h.s.) can be expressed by

$$\boldsymbol{J}_{\mathrm{v},i} = -\ \eta_i\ \mathrm{Grad}\ \upsilon \qquad (23)$$

where η_i is defined as a partial viscosity of the ith component. In general, the gradient of a vector quantity is a second order tensor.

The equation of momentum conservation can be derived from the general, already used, method. If momentum is an extensive property of the medium and υ_i is a specific value of momentum of the ith component, the time change of momentum, $\int \rho_i\upsilon_i\ \mathrm{d}V$, is given by*

$$\int_V \frac{\partial(\rho_i\upsilon_i)}{\partial t}\,\mathrm{d}V = -\int_A \rho_i\upsilon_i\upsilon\cdot\mathrm{d}A\ -\int_A \boldsymbol{J}_{\mathrm{v},i}\cdot\mathrm{d}A + \int_V \rho_i\boldsymbol{F}_{\mathrm{ext}}\mathrm{d}V + \int_V \rho_i\boldsymbol{F}_{\mathrm{int},i}\mathrm{d}V + \int_V \gamma_i\mathrm{d}V \qquad (24)$$

The first term on the r.h.s. is the drift flow of momentum out of the V through the surface of the volume element, the second term represents the kinematic forces acting on the V (the momentum exchange due to viscosity). These two terms represent the contribution from the kinematic pressure and internal

---

* Traditional, and commonly up to now accepted, form of the balance equation for the rate of change of momentum is written

friction (the contribution, which relative to the centre of mass, can be expressed by the kinematic pressure tensor, Π. The last term on the r.h.s.

$$\int_V \frac{\partial(\rho_i \upsilon_i)}{\partial t}\,\mathrm{d}V = -\int_A \rho_i \upsilon_i \upsilon_i \bullet \mathrm{d}A - \int_A \boldsymbol{J}_{v,i} \bullet \mathrm{d}A + \int_V \rho_i \boldsymbol{F}_{\mathrm{ext}}\,\mathrm{d}V + \int_V \rho_i \boldsymbol{F}_{\mathrm{int},i}\,\mathrm{d}V + \int_V \gamma_i\,\mathrm{d}V$$

Thus the principal difference between the two formulas is the result of defining eq. (2) and, can be seen upon comparison of the first terms on the r.h.s. of the eq. (24) and the classical, written above formula. In the traditional treatments it is always postulated that momentum is transported by the local average velocity, $\boldsymbol{u}_i$. The traditional approach results in the equation of motion in the form [an scrupulous reader may return to this point after following the derivation of the differential form of eq. (24)]:

$$\rho \left.\frac{D\boldsymbol{u}}{Dt}\right|_{\boldsymbol{u}} = -\mathrm{Div} \sum_{i=1}^{n} \boldsymbol{J}_{\mathrm{v},i} + \rho \boldsymbol{F}_{\mathrm{ext}} - \mathrm{grad} p$$

Thus the traditional equation of motion does not contain [compare also eq. (31)] the Div ($\boldsymbol{j}_d \boldsymbol{u}$) term.

Physically it means that, the motion as a result of diffusional matter transport is excluded in the all earlier approaches. Namely such a classical formulas do not allow to calculate: i) the time dependence of the Kirkendall effect (in solids), ii) the flow induced by the mutual diffusion in liquids and, iii) the diffusion induced drift ("convection") in multicomponent gas mixtures.

The final consequence of such a restriction (in the classical formulas of the equation of motion) is their bypass in chemistry and in the majority of present treatments on the diffusional mass transport, *e.g.* in solids, represents a contribution from the rate of momentum increase per unit volume, γ_i, as a result of momentum exchange with the other diffusing components. Because the total momentum is conserved: $\sum \gamma_i = 0$. The external and internal forcings are represented by the third and fourth terms, respectively. The internal forcing represents contribution from the internal potential energy due to molecular interactions and consequently eq. (24) can be written in the form

$$\int_V \frac{\partial(\rho_i \upsilon_i)}{\partial t}\,\mathrm{d}V = -\int_A \rho_i \upsilon_i \upsilon \bullet \mathrm{d}A - \int_A \boldsymbol{J}_{v,i} \bullet \mathrm{d}A + \int_V \rho_i \boldsymbol{F}_{\mathrm{ext}}\,\mathrm{d}V + \int_{\mathrm{A}} \mathrm{grad}\left(\frac{\partial U_{\mathrm{I},i}}{\partial V}\right)\mathrm{d}V + \int_V \gamma_i\,\mathrm{d}V \tag{25}$$

It follows that the internal forcing can be expressed by the gradient of the partial hydrostatic pressure of the *i*th component (p_i), where the local hydrostatic pressure is: $p = \sum_{i=1}^{n} \rho_i$ and,

$$\mathrm{grad}\, p_i = -\mathrm{grad}\left(\frac{\partial U_{\mathrm{I},i}}{\partial V}\right) \tag{26}$$

where $U_{I,i}$ is the internal energy of *i*th component. Thus, after transforming the surface integrals of eq. (25) to volume integrals by Gauss' theorem and nothing that the resulting integrand is zero, the equation of momentum conservation of the *i*th component becomes

$$\frac{\partial(\rho_i \upsilon_i)}{\partial t} = -\mathrm{Div}\,(\rho_i \upsilon_i \upsilon) - \mathrm{Div}\,\boldsymbol{J}_{\mathrm{v},i} + \rho_i \boldsymbol{F}_{\mathrm{ext}} - \mathrm{grad}\, p_i + \gamma_i \tag{27}$$

In the case of a n-component nonuniform single phase medium, the equation of momentum conservation for the medium as a whole (*i.e.* equation of motion, ME) is obtained upon adding all the eqs. (27), viz.,

$$\frac{\partial(\rho \boldsymbol{u})}{\partial t} = -\mathrm{Div}\,(\rho\, \boldsymbol{u}\, \upsilon) - \mathrm{Div} \sum_{i=1}^{n} \boldsymbol{J}_{\mathrm{v},i} + \rho \boldsymbol{F}_{\mathrm{ext}} - \mathrm{grad} \sum_{i=1}^{n} p_i \tag{28}$$

The ME can be rearranged to

$$\rho\left(\frac{\partial \boldsymbol{u}}{\partial t} + \upsilon \bullet \mathrm{Grad}\, \boldsymbol{u}\right) + \boldsymbol{u}\left[\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho\, \upsilon)\right] = -\mathrm{Div} \sum_{i=1}^{n} \boldsymbol{J}_{\mathrm{v},i} + \rho\, \boldsymbol{F}_{\mathrm{ext}} - \mathrm{grad}\, p \tag{29}$$

which upon substituting eqs. (11) and (20) becomes finally:

$$\rho \left.\frac{D\boldsymbol{u}}{Dt}\right|_{\upsilon} = \boldsymbol{u}\, \mathrm{div}\, \boldsymbol{j}_{\mathrm{d}} - \mathrm{Div} \sum_{i=1}^{n} \boldsymbol{J}_{\mathrm{v},i} + \rho \boldsymbol{F}_{\mathrm{ext}} - \mathrm{grad} p \tag{30}$$

Upon expressing the equation of motion relative to the centre of mass velocity it takes form

$$\rho \frac{Du}{Dt}\bigg|_u = \mathrm{Div}(\boldsymbol{j}_d \boldsymbol{u}) - \mathrm{Div}\sum_{i=1}^{n} \boldsymbol{J}_{v,i} + \rho \boldsymbol{F}_{ext} - \mathrm{grad}p \qquad (31)$$

Thus the net force acting on a volume element is a results of i) the outflow of momentum carried by the net diffusional flux, ii) the net inflow of momentum into the volume element due to the nonuniform field of the drift velocity within a medium and, iii) the internal and external forcing. The momentum flux is a second order tensor completely determined by the fluid (medium) properties and by the velocity and density fields. Equations (31) can be written in the standard form

$$\rho \frac{Du}{Dt}\bigg|_u + \mathrm{Div}\,\Pi + \mathrm{grad}\,p = \rho \boldsymbol{F}_{ext} \qquad (32)$$

where the kinematic pressure tensor is given by:

$$\Pi = \sum_{i=1}^{n} \boldsymbol{J}_{v,i} - \left(\sum_{i=1}^{n} j_{d,i}\right) \boldsymbol{u} = \boldsymbol{J}_v - \boldsymbol{j}_d\,\boldsymbol{u} \qquad (33)$$

In the case of a single component compressible fluid the kinematic pressure tensor has a form

$$\Pi = \boldsymbol{J}_v - \boldsymbol{j}_d\,\boldsymbol{u} \qquad (34)$$

Note that:

1) when the ME is written for a single component, ideal fluid at equilibrium (where the velocity, temperature and density gradients are absent from the fluid), the contribution to Π from viscous and diffusion effects vanishes and $\Pi = 0$. The ME, eq. (32), becomes, in this case,

$$\rho \frac{Du}{Dt}\bigg|_u + \mathrm{grad}\,p = \rho \boldsymbol{F}_{ext} \qquad (35)$$

which is well-known Euler's equation for an ideal non-compressible fluid.

2) In the simplified case of an isothermal diffusional transport in solids (namely when the external forcings stresses and plastic deformation are negligible when compared to the chemical forcing) the ME, eq. (30), reduces to

$$\rho \frac{Du}{Dt}\bigg|_v = \boldsymbol{u}\,\mathrm{div}\,\boldsymbol{j}_d \qquad (36)$$

The derivation and the practical application of this form of the ME has been already published[8].

3) In the case of an ideal gas atmosphere the hydrostatic pressure term vanishes ($\partial U_1/\partial V = 0$) and the ME, eq. (32), becomes:

$$\rho \frac{Du}{Dt}\bigg|_u + \mathrm{Div}\,\Pi = \rho \boldsymbol{F}_{ext} \qquad (37)$$

The derived equations (CE and ME) allow to obtain a very convenient secondary relations.

Rate of change of potential energy. The potential energy ψ of the medium which moves in the field of a conservative external force $\boldsymbol{F}_{ext}$ is defined by

$$\boldsymbol{F}_{ext} = -\ \mathrm{grad}\ \psi \qquad (38)$$

For the example considered here (*i.e.* stationary external force field) it is:

$$\frac{\partial \psi}{\partial t} = 0 \qquad (39)$$

The equation for the change of potential energy is obtained by multiplying the equation of continuity [eq. (21) written in the ERF] by ψ, with the result,

$$\frac{\partial(\rho\,\psi)}{\partial t} = -\,\psi\,\mathrm{div}\,(\rho\,\boldsymbol{u}) \qquad (40)$$

and in the IRF [using eqs. (9), (10) and (21)], it is

$$\rho\,\frac{D\psi}{Dt}\bigg|_u = \rho\,\boldsymbol{u}\cdot\mathrm{grad}\,\psi \qquad (41)$$

Rate of change of kinetic energy. The ME allows one to obtain the rate of change of kinetic energy. If the ME, eq. (32), is multiplied by $\boldsymbol{u}$, it becomes the equation of the kinetic energy conservation,

$$\frac{1}{2}\,\rho\,\frac{Du^2}{Dt}\bigg|_u = -\,\boldsymbol{u}\cdot\mathrm{Div}\Pi + \rho\,\boldsymbol{u}\cdot\boldsymbol{F}_{ext} - \boldsymbol{u}\cdot\mathrm{grad}\,p \qquad (42)$$

In general the kinetic energy is not conserved as a result of the energy dissipation due to the diffusion and viscosity (kinematic pressure tensor, Π).

Conservation of internal energy

In deriving the mathematical formula of internal energy conservation it is assumed that: i) the pressure and internal energy distribution may be determined within a medium, ii) the work and energy (heat) transfer of the process formed by two successive processes is the sum of both processes and, iii) it is possible to connect two arbitrary states by some process.

If u_I is defined as the internal specific energy per unit mass (it contains contribution from the internal thermal kinetic energy and from internal potential energy due to molecular interactions), the equation for the conservation of internal energy can be derived from the already used general method. The time change of u_I is given by

$$\int_V \frac{\partial(\mathrm{r}\, u_I)}{\partial t} \mathrm{d}V =$$

$$-\int_A \rho\, u_I \boldsymbol{u} \bullet \mathrm{d}A - \int_A \boldsymbol{j}_q \bullet \mathrm{d}A - \int_V p \operatorname{div} \boldsymbol{u}\, \mathrm{d}V - \int_V \Pi \bullet \operatorname{Grad} \boldsymbol{u}\, \mathrm{d}V - \int_V \rho\, \upsilon_d \bullet \operatorname{grad}\psi\, \mathrm{d}V$$

$$\left[\begin{array}{c}\text{flow of}\\\text{internal}\\\text{energy,}\\\text{ERF}\end{array}\right] + \left[\begin{array}{c}\text{thermal}\\\text{energy}\\\text{flux,}\\\text{ERF=}\\\text{IRF}\end{array}\right] + \left[\begin{array}{c}\text{work perfor-}\\\text{med on the}\\\text{volume ele-}\\\text{ment by the}\\\text{hydrostatic}\\\text{presure,}\\\text{ERF=IRF}\end{array}\right] + \left[\begin{array}{c}\text{work performed}\\\text{on the volume}\\\text{element by the}\\\text{kinematic}\\\text{pressure,}\\\text{ERF=IRF}\end{array}\right] + \left[\begin{array}{c}\text{work per-}\\\text{formed in}\\\text{the volume}\\\text{element by}\\\text{external}\\\text{forcing,}\\\text{ERF=IRF}\end{array}\right] \tag{43}$$

where the heat is defined as the entity which flows between regions of different temperatures solely because these regions are at different temperatures. There is no unique way to split the heat flux into the purely conducting term, j_q, and the diffusion term (representing the energy flow due to the diffusion of mass). The formal eq. (43), however, is sufficient to define j_q as a term representing the energy flux due to all mechanisms except the energy flow due to the mass transport. The coefficient of thermal conductivity is defined by the relation

$$j_q = -\lambda \operatorname{grad} T \tag{44}$$

where λ is the coefficient of thermal conductivity.

Thus, after transforming the surface integral of eq. (43) to volume integral by Gauss' theorem and nothing that the resulting integrand is zero, the equation of internal energy conservation becomes

$$\frac{\partial(\rho\, u_I)}{\partial t} = -\operatorname{div}(\rho\, u_I \boldsymbol{u}) - \operatorname{div}\boldsymbol{j}_q - p \operatorname{div} \boldsymbol{u} - \Pi \bullet \operatorname{Grad} \boldsymbol{u} - \rho\, \upsilon_d \bullet \operatorname{grad}\psi \tag{45}$$

This relation, with eqs. (9) and (21), becomes finally in IRF:

$$\left.\frac{\mathbf{D}u_I}{\mathbf{D}t}\right|_{\boldsymbol{u}} = -\frac{1}{\rho} \operatorname{div}\boldsymbol{j}_q - \frac{p}{\rho} \operatorname{div} \boldsymbol{u} - \frac{1}{\rho} \Pi \bullet \operatorname{Grad} \boldsymbol{u} - \upsilon_d \bullet \operatorname{grad}\psi \tag{46}$$

The internal energy is not conserved because of the presence of the terms $\Pi \cdot \operatorname{Grad} \boldsymbol{u}$, $p \operatorname{div} \boldsymbol{u}$ and $\rho\, \upsilon_d \cdot \operatorname{grad} \psi$, which represent dissipation of the kinetic, internal and potential energy, respectively.

When the viscosity, diffusion and drift velocity (medium expansion) are negligible the equation of the internal energy conservation reduces to the formula which is equivalent of the 2nd Fourier' law

$$\frac{\partial u_I}{\partial t} = -\frac{1}{\rho} \operatorname{div} \boldsymbol{j}_q \tag{47}$$

Equation (46) is formally the analogue of the classical formula$^{6)}$. Yet, the essential benefit of the present treatment results from the explicit definition of the kinematic pressure tensor.

In many experimental situations the local pressure is an interest. In open systems the measurable quantity is the local hydrodynamical pressure. The formal definition and the resulting method of determining this quantity is as follow.

Calculation of the local hydrodynamical pressure. The hydrodynamical pressure at a fixed moment t can be defined using the Hodge decomposition of the vector field to the solenoidal and conesrvative parts (namely it is a potential of the conservative part of the difference between a total force and an external force acting on a medium at the moment t). Thus the CE and derived conservation equations completely describe the transport.

The self-consistency of the derived equations with the thermodynamic aspects of the transport pehnomena is discussed in the last section.

DISCUSSION

Conservation of the total energy. The total energy is defined as the sum of three terms; the kinetic energy $1/2\ u^2$, the specific potential energy resulting from the external, conservative force ψ, and the internal specific energy u_I:

$$\boldsymbol{e} = \frac{1}{2} \boldsymbol{u}^2 + \boldsymbol{u}_I + \psi$$

where the term u_I contains the contribution from internal thermal kinetic energy and from the internal potential energy due to the molecular interaction. Because the equations for the potential energy, kinetic energy and internal energy have been already derived, thus the conservation for the total energy is obtained upon adding eqs. (41), (42) and (46), with a result:

$$\rho \left.\frac{\mathrm{D}e}{\mathrm{D}t}\right|_{\boldsymbol{u}} = -\operatorname{div}(p\boldsymbol{u} + \Pi \bullet \boldsymbol{u} + \boldsymbol{j}_{\mathrm{q}}) - \rho\, \upsilon_{\mathrm{d}} \bullet \operatorname{grad} \psi \quad (49)$$

Upon splitting the kinematic pressure tensor into two parts [equation (33)] it becomes finally (in the IRF):

$$\rho \left.\frac{\mathrm{D}e}{\mathrm{D}t}\right|_{\boldsymbol{u}} = -\operatorname{div}(p\boldsymbol{u} + \boldsymbol{j}_{\mathrm{q}} + \boldsymbol{J}_{\mathrm{v}}\boldsymbol{u} - \boldsymbol{j}_{\mathrm{d}}\boldsymbol{u}^2) - \boldsymbol{j}_{\mathrm{d}} \bullet \operatorname{grad} \psi \quad (50)$$

Conceivably contrary to common experience, the transport in gases is a most complex process. In general, none of the elementary processes (compressibility, diffusion and viscosity) becomes negligible and, as a consequence, only total energy is conserved.

In order to show the capability of the derived formulas in description of the transport, they will be markedly simplified now. The target is a detailed analysis of the transport in condensed compressible medium (e.g. simple fluids, amorphous solids, some poly-crystalline materials). Negligence of the dissipative processes in such a medium will result in a time independent, local (in IRF) formula of internal energy conservation. It will be shown that in such a "semi-ideal" media the I law results (*i.e.* I law is a local, time independent, formula of internal energy conservation in a non-viscous compressible media).

Conservation equations in a condensed medium. The further discussion will be restricted to the liquids and solids. In such systems the molecular transport (diffusion) is always a function of local gradients. Thus, eqs. (31), (46) and (50) can be written in the form (the all terms in which the differentials are multiplied become negligible):

$$\rho \left.\frac{\mathrm{D}\boldsymbol{u}}{\mathrm{D}t}\right|_{\boldsymbol{u}} = \boldsymbol{u} \operatorname{div} \boldsymbol{j}_{\mathrm{d}} - \operatorname{Div} \boldsymbol{J}_{\mathrm{v}} - \rho \operatorname{grad} \psi - \operatorname{grad} p \quad (51)$$

$$\rho \left.\frac{\mathrm{D}\boldsymbol{u}_{\mathrm{I}}}{\mathrm{D}t}\right|_{\boldsymbol{u}} = -\operatorname{div} \boldsymbol{j}_{\mathrm{q}} - p \operatorname{div} \boldsymbol{u} \quad (52)$$

$$\rho \left.\frac{\mathrm{D}e}{\mathrm{D}t}\right|_{\boldsymbol{u}} = -\operatorname{div}(p\boldsymbol{u} + \boldsymbol{j}_{\mathrm{q}}) - \boldsymbol{u} \bullet \operatorname{Div} \boldsymbol{J}_{\mathrm{v}} + \boldsymbol{u}^2 \operatorname{div} \boldsymbol{j}_{\mathrm{d}} \quad (53)$$

When diffusivity and viscosity are negligible (transport at low temperatures or some fast processes) the conservation equations can be further simplified to:

$$\rho \left.\frac{\mathrm{D}\boldsymbol{u}}{\mathrm{D}t}\right|_{\boldsymbol{u}} = -\rho \operatorname{grad} \psi - \operatorname{grad} p \quad (54)$$

The assumption that medium is at a close to equilibrium conditions, allows one to assume that the medium properties can be expressed by an equation of state. The arbitrary equation of state is convenient here to write in

$$\rho \left.\frac{\mathrm{D}\boldsymbol{u}_{\mathrm{I}}}{\mathrm{D}t}\right|_{\boldsymbol{u}} = -\operatorname{div} \boldsymbol{j}_{\mathrm{q}} - p \operatorname{div} \boldsymbol{u} \quad (55)$$

$$\rho \left.\frac{\mathrm{D}e}{\mathrm{D}t}\right|_{\boldsymbol{u}} = -\operatorname{div} \boldsymbol{j}_{\mathrm{q}} - \operatorname{div}(p\, \boldsymbol{u}) \quad (56)$$

the form of a quasi-linear relation between the density and pressure:

$$p = \boldsymbol{K}(\rho, \boldsymbol{T})\ \rho = \boldsymbol{K}\rho \quad (57)$$

where $\boldsymbol{K} = \left[\frac{\mathrm{J}}{\mathrm{kg}}\right] = \left[\frac{\mathrm{m}^2}{\mathrm{s}^2}\right]$ represents the internal energy per unit of mass (and in general can be a function of both the density and pressure).

The pressure, eq. (26), can be expressed now as a function of local variables which are used in the derived equations:

$$p = -\frac{\partial U_{\mathrm{I}}}{\partial V} = -\frac{\partial(\rho\, u_{\mathrm{I}} V)}{\partial V} = \rho^2 \frac{\partial u_{\mathrm{I}}}{\partial \rho} \quad (58)$$

and consequently from eqs. (57) and (58) it follows

$$\rho \frac{\partial u_{\mathrm{I}}}{\partial \rho} = K \quad (59)$$

$$\operatorname{grad} p = \rho \operatorname{grad} \boldsymbol{K} + \boldsymbol{K} \operatorname{grad} \rho \quad (60)$$

Equations (59) and (60) allow to express the pressure gradient as a function of the local variables:

$$\operatorname{grad} p = \rho \operatorname{grad} K + \rho \frac{\partial u_{\mathrm{I}}}{\partial \rho} \operatorname{grad} \rho = \quad (61)$$

$$= \rho \operatorname{grad} K + \rho \operatorname{grad} u_{\mathrm{I}}$$

Thus the chosen quasi-linear relation between the density and pressure allow, eq. (61), to write the equation of motion and the internal energy conservation equation in the Newtonian form:

$$\left.\frac{\mathbf{D}\boldsymbol{u}}{\mathbf{D}t}\right|_{u} = -\operatorname{grad}(K + u_{\mathrm{I}} + \psi) \tag{62}$$

$$\left.\frac{\mathbf{D}\boldsymbol{u}_{\mathrm{I}}}{\mathbf{D}t}\right|_{u} = -\frac{1}{\rho}\operatorname{div}\boldsymbol{j}_{\mathrm{q}} - \boldsymbol{K}\operatorname{div}\boldsymbol{u} \tag{63}$$

It is evident that when we know both the boundary and initial conditions the distributions of density, temperature and velocities can be calculated.

The equation of the total energy conservation in the discussed case can be written in the form:

$$\left.\frac{\mathbf{D}\boldsymbol{e}}{\mathbf{D}t}\right|_{u} = -\frac{1}{\rho}\operatorname{div}(\boldsymbol{K}\,\rho\,\boldsymbol{u}) - \frac{1}{\rho}\operatorname{div}\boldsymbol{j}_{\mathrm{q}} =$$

$$= -\frac{1}{\rho}\,\boldsymbol{u}\cdot\operatorname{grad}(\boldsymbol{K}\,\rho) - \boldsymbol{K}\operatorname{div}\boldsymbol{u} - \frac{1}{\rho}\operatorname{div}\boldsymbol{j}_{\mathrm{q}} \tag{64}$$

The equation of kinetic energy conservation, eq. (42), in the discussed case reduces to:

$$\left.\frac{\mathbf{D}\left(\frac{1}{2}\,\boldsymbol{u}^{2}\right)}{\mathbf{D}t}\right|_{u} = -\boldsymbol{u}\cdot\operatorname{grad}\psi - \frac{1}{\rho}\boldsymbol{u}\cdot\operatorname{grad}(\boldsymbol{K}\,\rho) \tag{65}$$

Thus, upon substituting into the first and second terms on the r.h.s. of the eq. (64), the derived relations [eqs. (65) and (21)] the continuity equation of the total energy in the medium becomes

$$\left.\frac{\mathbf{D}\left(\boldsymbol{u}_{\mathrm{I}} + \frac{1}{2}\,\boldsymbol{u}^{2} + \psi\right)}{\mathbf{D}t}\right|_{u} = \left.\frac{\mathbf{D}\left(\frac{1}{2}\,\boldsymbol{u}^{2}\right)}{\mathbf{D}t}\right|_{u} + \boldsymbol{u}\cdot\operatorname{grad}\psi$$

$$+\frac{K}{\rho}\left.\frac{\mathbf{D}\rho}{\mathbf{D}t}\right|_{u} - \frac{1}{\rho}\operatorname{div}\boldsymbol{j}_{\mathrm{q}} \tag{66}$$

Upon taking into account the equation of the potential energy conservation, eq. (41), it finally reduces to:

$$\left.\frac{\mathbf{D}\boldsymbol{u}_{\mathrm{I}}}{\mathbf{D}t}\right|_{u} = \boldsymbol{K}\left.\frac{\mathbf{D}\ln\rho}{\mathbf{D}t}\right|_{u} - \frac{1}{\rho}\operatorname{div}\boldsymbol{j}_{\mathrm{q}} \tag{67}$$

Thus in the IRF, for an arbitrary time period δt, it is:

$$du_{\mathrm{I}} = K\,\delta\ln\rho + \delta q$$

$$du_{\mathrm{I}} = \delta\,w + \delta q \tag{68}$$

It follows that in the compressible media (when diffusivity and viscosity are negligible) and in the IRF the derived formulas result in the classical formula of the I law. In the other words, internal energy is conserved in the media in which dissipative processes are negligible.

In the ERF the equation of total energy conservation reads:

$$\frac{\partial u_{\mathrm{I}}}{\partial t} - K\,\frac{\partial\ln\rho}{\partial t} + \frac{1}{\rho}\operatorname{div}\boldsymbol{j}_{\mathrm{q}} = \boldsymbol{u}\cdot(\boldsymbol{K}\operatorname{grad}\ln\rho - \operatorname{grad}u_{\mathrm{I}}) \tag{69}$$

SUMMARY

The transport in the viscous, compressible media in the field of the conservative force, is described by the following conservation equations:

$$\left.\frac{\mathbf{D}\rho}{\mathbf{D}t}\right|_{u} + \rho\operatorname{div}u = 0$$

$$\rho\left.\frac{\mathbf{D}\boldsymbol{u}}{\mathbf{D}t}\right|_{u} + \operatorname{Div}\Pi + \operatorname{grad}p = -\rho\ \mathrm{gead}\,\psi$$

$$\rho\left.\frac{\mathbf{D}u}{\mathbf{D}t}\right|_{u} + \rho\,\upsilon_{\mathrm{d}}\cdot\operatorname{grad}\psi + p\operatorname{div}\boldsymbol{u} + \Pi\cdot\operatorname{Grad}\boldsymbol{u} = -\operatorname{div}\boldsymbol{j}_{\mathrm{q}}$$

where the equation of state relates the internal specific energy, density and temperature. The hydrostatic pressure and the kinematic pressure are defined by:

$$p = -\frac{\partial U_{\mathrm{I}}}{\partial V}$$

$$\Pi = \boldsymbol{J}_{\mathrm{v}} - \boldsymbol{j}_{\mathrm{d}}\,\boldsymbol{u}$$

The fluxes of mass, momentum and heat can be expressed by any appropriate formulas, *e.g.*:

$$\boldsymbol{j}_{d,i} = \rho_i\upsilon_{d,i} = -\boldsymbol{D}_i\operatorname{grad}\rho_i$$

$$J_{v,i} = -\eta_i \, \mathrm{Grad}\, \upsilon$$

$$j_q = -\lambda \, \mathrm{grad}\, T$$

ACKNOWLEDGMENTS

Support of the Tokyo Institute of Technology and of the Polish State Committee for Scientific Research in the course of this work is acknowledged with gratitude. The author is genuinely indebted to Prof. M. Wakihara (TIT) and Dr. K. Holly (Cracow) for their patience with author many queries, numerous discussions and words of encouragement.

References

1) H-O, Kreiss and J. Lorentz, *Initial-Boundary Value Problems of the Navier-Stokes Equations* (Academic Press Inc., San Diego 1989).

2) I. Samohyl, *Thermodynamics of Irreversible Processes in Fluid Mixtures (Approached by Rational Thermodynamics),* Teubner-Texte zur Physik, Band **12**, 10 (1987).

3) L.S. Darken, *Trans, AIME*, **174**, 184 (1948).

4) K. Holly, *Universitatis Jagiellonicae Acta Mathematica*, **28**, 135 (1991).

5) M. Danielewski, *Defect and Diffusion Data*, In press.

6) H.J.M. Hanley, *Transport Phenomena in Fluids* (Marcel Dekker, New York 1969).

7) M. Danielewski, *Diffusion in Solids and High Temperature Oxidation of Metals*, J. Nowotny ed. (Trans Tech Publications, Zurich 1992).

8) M. Danielewski, *Phenomenology of interdiffusion in solids, conservation of momentum and equation of motion*, in *Defect and Diffusion Data*, in press.

要　旨

開放系での運動方程式とエネルギー保存

熱移動および物質移動の動力学に関する記述について新しい提案をする。非平衡における均質多成分系の輸送に対し新たにモーメンタム流束に関する表現を導入した。

この方法は種々の保存方程式に対応でき，Fickの第二法則やFourierの法則の適用限界を明らかにし，また実験から得られる結果がどのように応用できるかを示唆する。